ARES NO_x Sensor Development

Los Alamos National Laboratory

Eric L. Brosha, R. Mukundan, and Roger Lujan , Research Staff

Fernando H. Garzon, Sensor Project Leader

Materials Science and Technology Division
Electrochemical Materials and Devices Group, MST-11

Project Description, Goals, and Objectives

- Develop new, lost cost, solid-state sensors to detect NO_x in the exhaust gas stream of a reciprocating engine.
  - Ceramic sensors that operate on electrochemical principles
- Sensors to control regenerative NO_x catalyst systems.
- Sensors must be inexpensive, robust, and be able to detect NO_x in regimes of PO_2, T, $[NO_x]$ characteristic of current engine technology
- Lifetime, stability, sensitivity, response time, sulfur tolerance, device reproducibility, cost, etc.

Los Alamos NATIONAL LABORATORY

Project Team - LANL

- LANL team has 10 years of experience in the development of gas sensor technology
  - Oxygen
  - Sulfur dioxide
  - Hydrocarbons
  - Carbon monoxide
  - Nitric oxides

- LANL CRADA with USCAR to develop high temperature electrochemical sensors for OBD-II applications.
- FY 1997 - 2001

  Sensors required to measure real-time NMHC concentration

  Partners: Ford, GM, and Chrysler

- 4 Patents issued in sensor technology

Los Alamos NATIONAL LABORATORY

Project Team

- Previous LANL sensor work examples:
  - LDRD sensor development work
    - "Controlled Interface Gas Sensors", U.S. Patent applied for 2002.
  - Sulfur resistant O_2 combustion control sensors
    - Winner 1999 R&D 100 award in collaboration with Rosemount Analytical Co.
    - U.S. Patent no. 6,277,256
  - Amperometric response, lean burn O_2 sensor work in collaboration with Delphi Automotive
    - U.S. Patents 5,695,624 & 5,543,025

- University Collaboration : ARES NO_x sensor development work performed in collaboration with Dr. Eric Wachsman and his sensor team at the University of Florida

Los Alamos NATIONAL LABORATORY

Impact on Goals of ARES Program

- Advanced reciprocating engines require new sensor technologies to reduce emissions and improve over-all efficiency.
  - NO_x emissions monitoring and control
  - Engine control
  - Control of NO_x regeneration catalysts and systems
- E.g. NO_x emissions cannot exceed 50 - 150 ppm (0.1 g/hp-hr).
- A NO_x sensor is needed to monitor and control emissions systems.
- Currently there is no suitable sensing technology available that is low-cost sulfur tolerant, long-lifetime, etc.

ARES Emissions Information

Event Comment		Lean Limit				Detonation Limit
Engine Speed	rev/min	1499	1499	1500	1500	1500
Air/Fuel Stoich	kg air/kg fuel	16.04	16.04	16.04	16.04	16.05
Air/Fuel Ratio	kg air/kg fuel	31.65	30.09	29.35	28.88	28.17
Equivalence Ratio	none	0.51	0.53	0.55	0.56	0.57
Turbocharger Efficiency	%	64.02	64.30	64.60	64.68	65.01
Oxides of Nitrogen	ppm	35	141	280	445	872
Carbon Monoxide	ppm	441	376	405	432	472
Carbon Dioxide	%	5.99	6.45	6.59	6.75	6.95
Unburned Hydrocarbons	ppm	2413	1758	1636	1565	1457
Exhaust Oxygen Content	%	10.86	10.09	9.83	9.55	9.19

Table 1. Exhaust gas data for advanced reciprocating engines operating under differing conditions.

- NO_x sensors need to operate in an environment with oxygen, HC's (CH_4), carbon dioxide, and carbon monoxide

Los Alamos NATIONAL LABORATORY

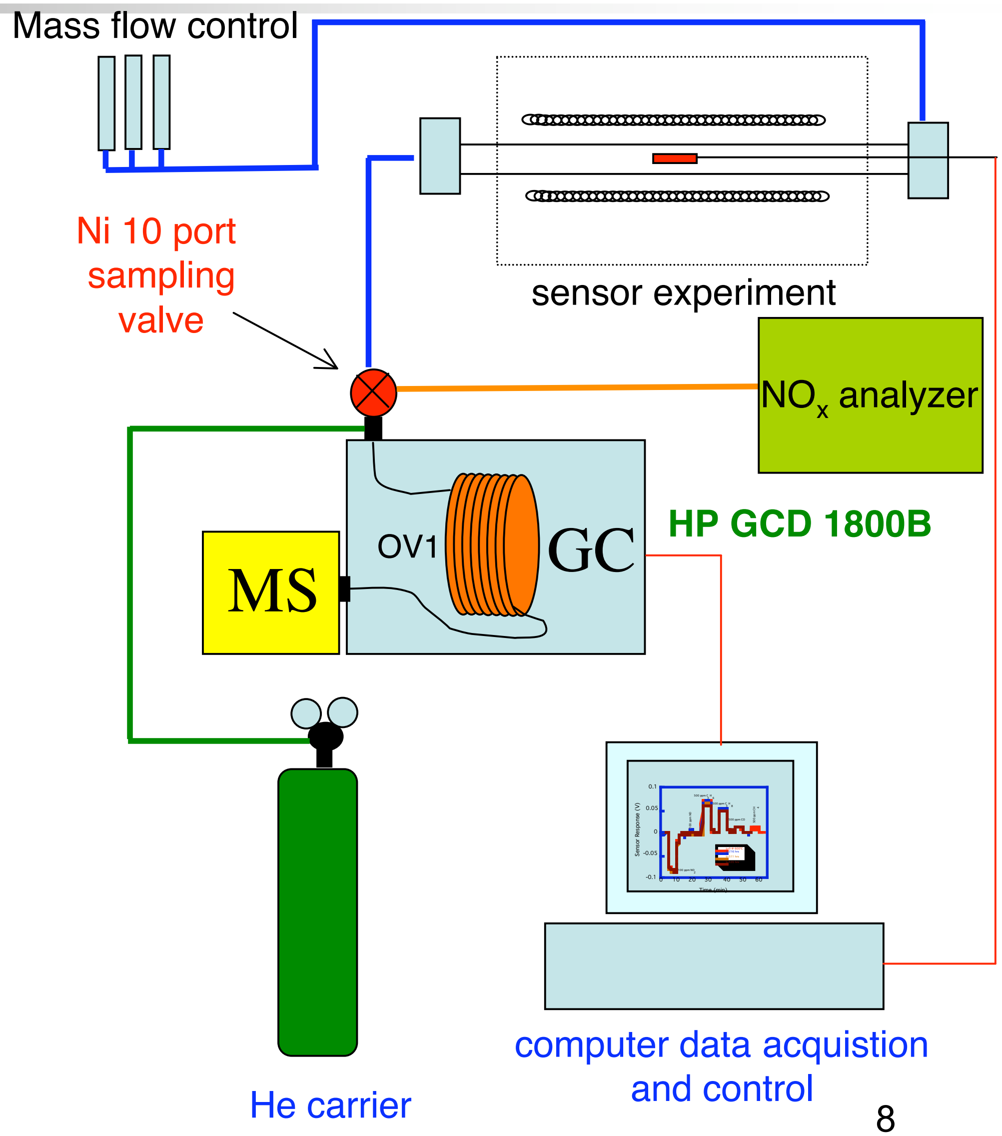
Milestones completed and planned

- Assemble analytical NOx capability at LANL with resources that are available. Completed
- Fabricate devices for initial study to demonstrate proof-of-concept. Completed
- Test and calibrate analytical [NO_x] system and build new test stations. Completed
- Study factors that affect sensitivity, lifetime, response time. Work In Progress
- Study electrode materials - NO_x catalysis and electrocatalysis. Work In Progress
- Study electro-catalysis and NO_x mixed potential electrochemistry. Work In Progress
- Improve NO_x sensor.Work In Progress
- Identify industrial partners for sensor commercialization. Work In Progress

Los Alamos NATIONAL LABORATORY

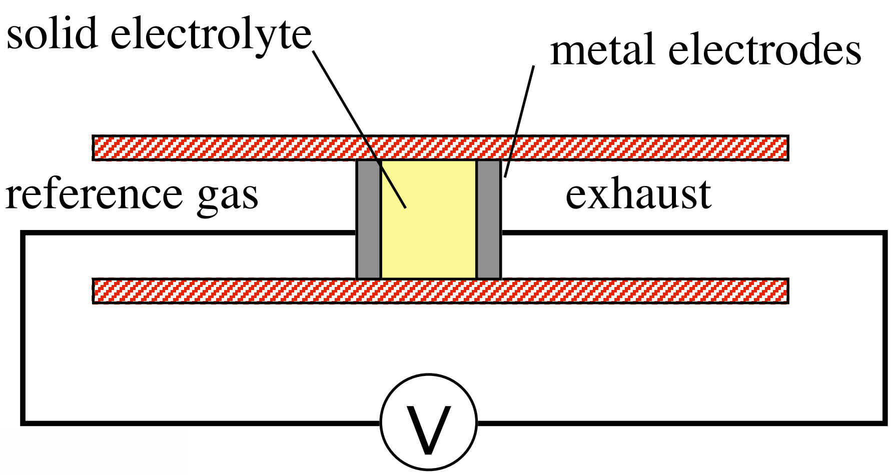
Development of NO_x Analysis Capability

- Develop NO_x and interference gas analysis system
- First task was to build an in-house NO_x measurement capability.
  - $[NO_x]$ changes over time
  - Complex equilibrium in presence of O_2
- Horriba analyzer for NO_x
- GC/MS system used to characterize interference gas concentrations



Nernstian Sensor Response

- Oxygen ion electrolyte, Pt electrodes
  - $t_{ion} >> t_e$
- Nernst equation obeyed if only oxygen is involved in electrochemical reactions
  - Oxygen- nitrogen mixtures



$$E = \frac{RT}{4F} \ln \left(\frac{P'_{O_2}}{P''_{O_2}} \right)$$

Sensor Theory (Interfaces)

- Zirconium oxide is doped with yttrium oxide to produce lattice vacancies:

$$ZrO_2 + {}_xY_2O_3 \rightarrow Zr_{1-2x}Y_{2x}O_{2-x}$$

$${}_xY \xrightarrow[ZrO_2]{} {}_xY'_{Zr} + \tfrac{x}{2}V_O^{**}$$

- defects in zirconia electrolytes are charged:

$$\frac{1}{2}O_{2(g)} + V_O^{**} \xleftrightarrow[ZrO_2]{} O_O^x + 2h^*$$

- Surface concentration of vacancies are much lower than bulk in air
  - Minority electronic carriers present at surface can diffuse across solid electrolyte/electrode interface

$$E_{F(elect)} = \mu_e + zq\phi$$

$$j_D + j_\phi = 0$$

$$0 = c\frac{D}{kT}\frac{d\mu}{dx} + \frac{zqD}{kT}c\frac{d\phi}{dx}$$

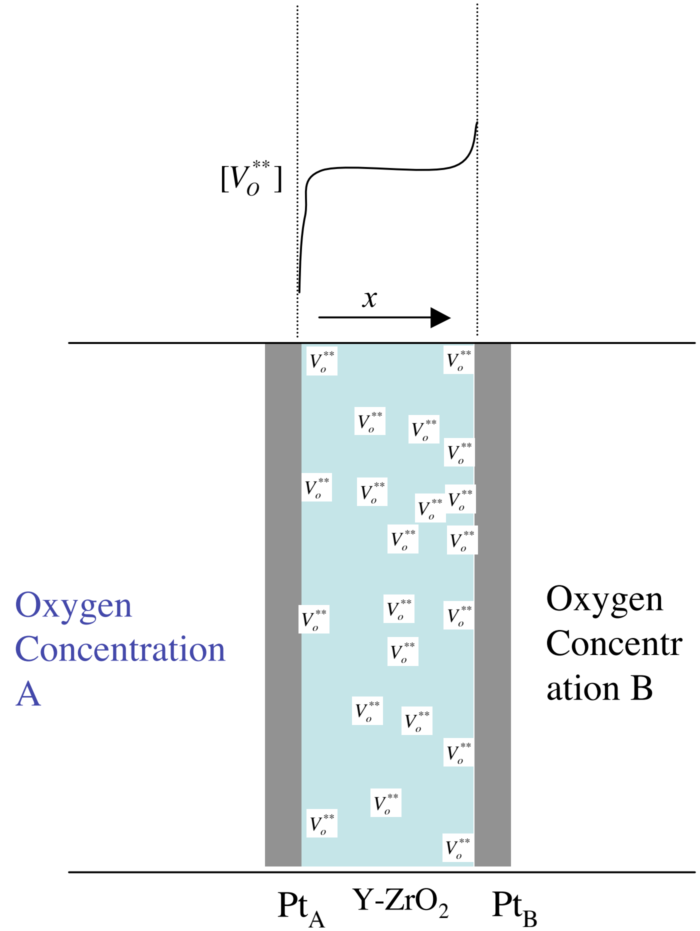
Sensor Theory

- Charged defect activity and concentration at surfaces controlled by chemical eq.

$$\frac{1}{2}O_{2(g)} + V_O^{**} + 2e^- \xleftrightarrow[Pt/ZrO_2]{} O_O^x$$

$$\Delta\phi_{Pt,AB} = \frac{RT}{nF}\ln\frac{(a_{O_2,PtB})}{(a_{O_2,PtA})} = \frac{RT}{nF}\ln\frac{(a_{V_O^{**}(ZrO_2,B)})}{(a_{V_O^{**}(ZrO_2,A)})}$$

$$a_{V_O^{**}(ZrO_2)} = \gamma[V_O^{**}]$$



Multiple Redox Gases

- More than one reaction can control charged species activities at sensor interfaces:

$$\frac{1}{2}O_2 + V_O^{\cdot\cdot} + 2e^{'} \leftrightarrow O_O$$

$$NO + O_O \leftrightarrow NO_2 + V_O^{\cdot\cdot} + 2e^{'}$$

- Reactions need to be divided into elementary steps with kinetic rate constants k_i
- Extremely complex due large number of elementary reaction steps

Los Alamos
NATIONAL LABORATORY

Reactions Before Triple Phase Boundary

•As the gases diffuse to triple phase boundaries chemical reactions change gas concentrations

-gas diffusion rates and mechanisms

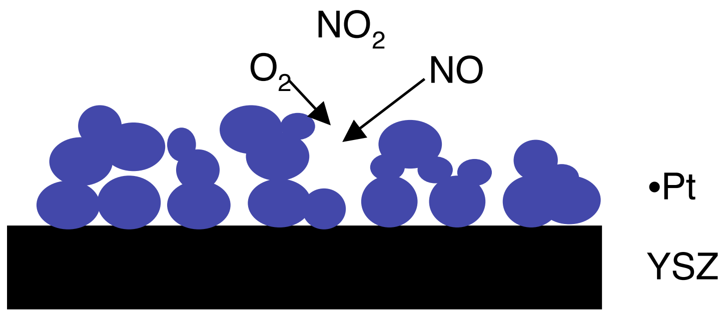
$$D \propto \sqrt{m_g / kT}$$

–homogeneous reaction rates

$$NO_{(g)} + \frac{1}{2} O_{2(g)} \rightarrow NO_{2(g)}$$

–heterogeneous reaction rates

$$NO_{(ad)} + \frac{1}{2} O_{2(ad)} \xrightarrow[Pt]{} NO_{2(g)}$$



Mixed Potential Representation Of Reaction Rates Near TPB

•For multiple parallel redox processes the potential of the electrode is determined by kinetic reaction rate constants (*k*) and activities (*a*) of the individual species:

$$\sum u_{ij} O_j + n_i e^- \rightarrow \sum v_{il} R_l$$

$$\Delta\phi_{electrode} = \left[\frac{RT}{nF} \ln \frac{\sum k_{ri} \prod a_{O_j}^{u_{ij}}}{\sum k_{oi} \prod a_{R_l}^{v_{il}}} \right]$$

•Many of the elementary rate constants are included in the redox reaction rate constants

•For a zirconia sensor the interfacial concentration of charged species is controlled by the triple phase boundary reaction rate kinetics

Los Alamos NATIONAL LABORATORY

Kinetic Devices

- Exploit the differences in electrode reaction rate kinetics with electrolyte ion to increase sensitivity to target gas
- Knowledge of electrode catalysis reactions needed
- Need electrode materials with high rate constants *k* for nitric oxide reactions for sensing electrode
  - Perovskite oxides: ABO_3
  - Spinel oxides: AB_2O_4
- Lanthanum chromium oxide perovskites $LaMCrO_3$ compounds
  - M=Mg, Ca, or Sr
- Spinels: $ZnFe_2O_4$, $NiCr_2O_4$

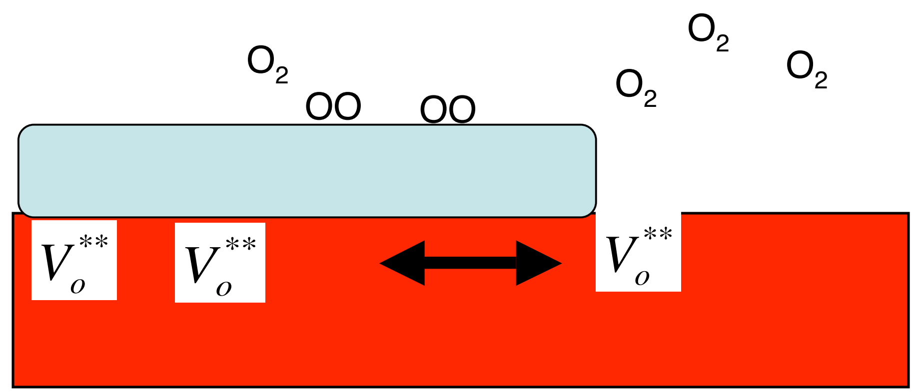
$$\frac{1}{2}O_{2(g)} + V_O^{**} + 2e^- \underset{\leftarrow k_{O\,ox}}{\overset{k_{O_2 red}\rightarrow}{\Longleftrightarrow}} O_o$$

$$NO_{2(gas)} + V_o^{**} + 2e^- \underset{\leftarrow k_{NO\,ox}}{\overset{k_{NO_2 red}\rightarrow}{\Longleftrightarrow}} NO_{(gas)} + O_o$$

Sensor Response Kinetics

- Rate determining steps:
  - Adsorption of Oxygen
  - Diffusion to TPB
  - Charge transfer
  - Diffusion of oxide ions, holes along Pt electrode/electrolyte interface to equilibrate potential

- Diffusion of oxide ions via a vacancy mechanism to/from triple phase interface rate limiting in most cases
  - Fine grain size porous electrodes respond fastest



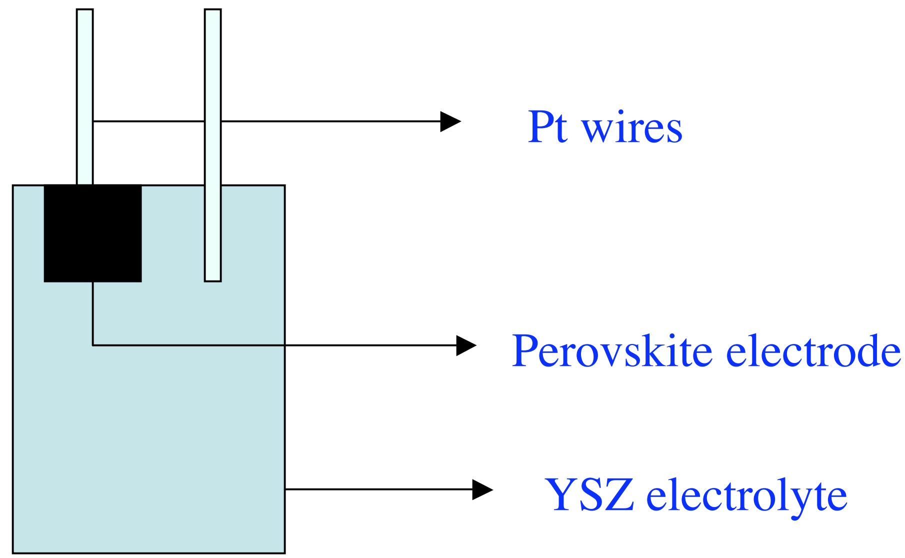
$$\frac{1}{2}O_2 + V_O^{\cdot\cdot} + 2e' \leftrightarrow O_O$$

$$\tau_{sensor} \propto \frac{x^2}{D}$$

Los Alamos
NATIONAL LABORATORY

Sensor Design

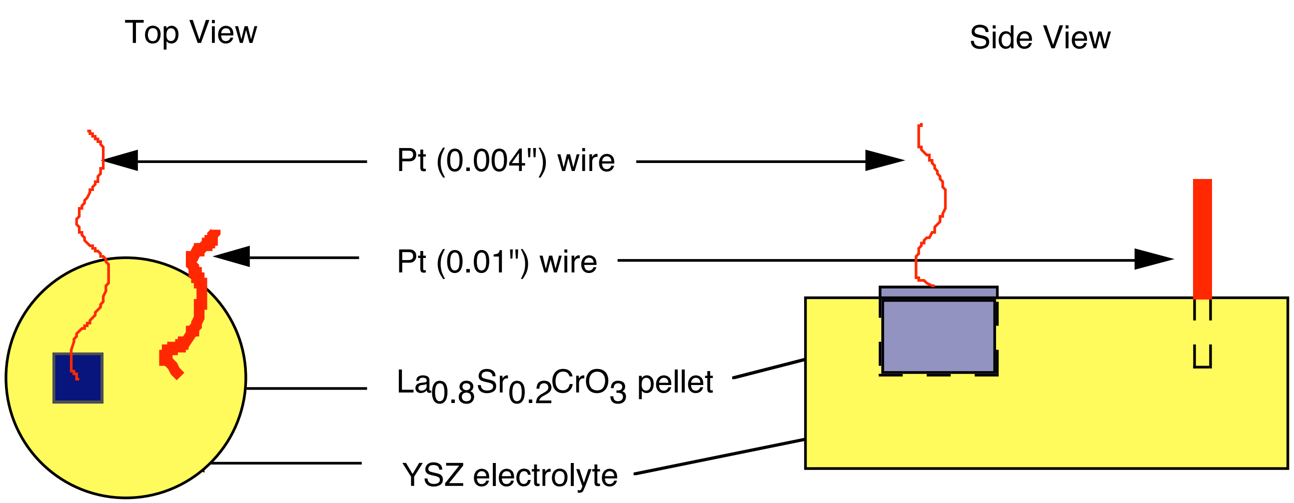
- Controlled Interface



- Wire and pellet electrodes in an electrolyte pellet
  - Stable, defined 3 phase interface

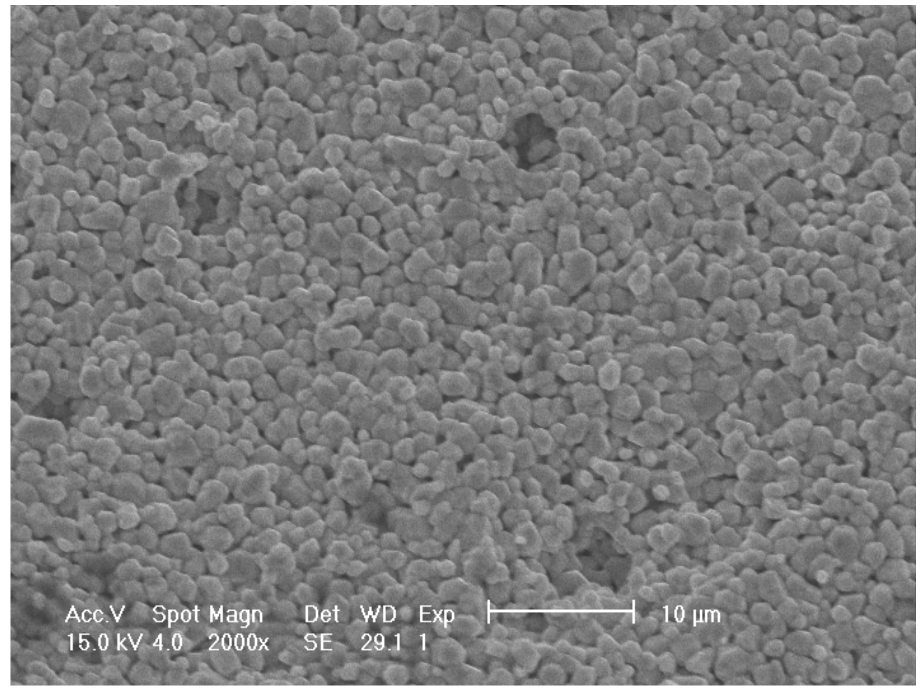
Sensor Design

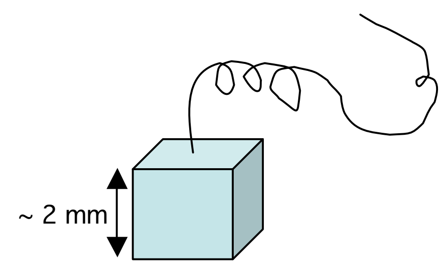
- Control the three-phase interface and surface area by pressing a dense pellet of $La_{0.8}Sr_{0.2}CrO_3$ and a Pt-wire into YSZ and co-sintering



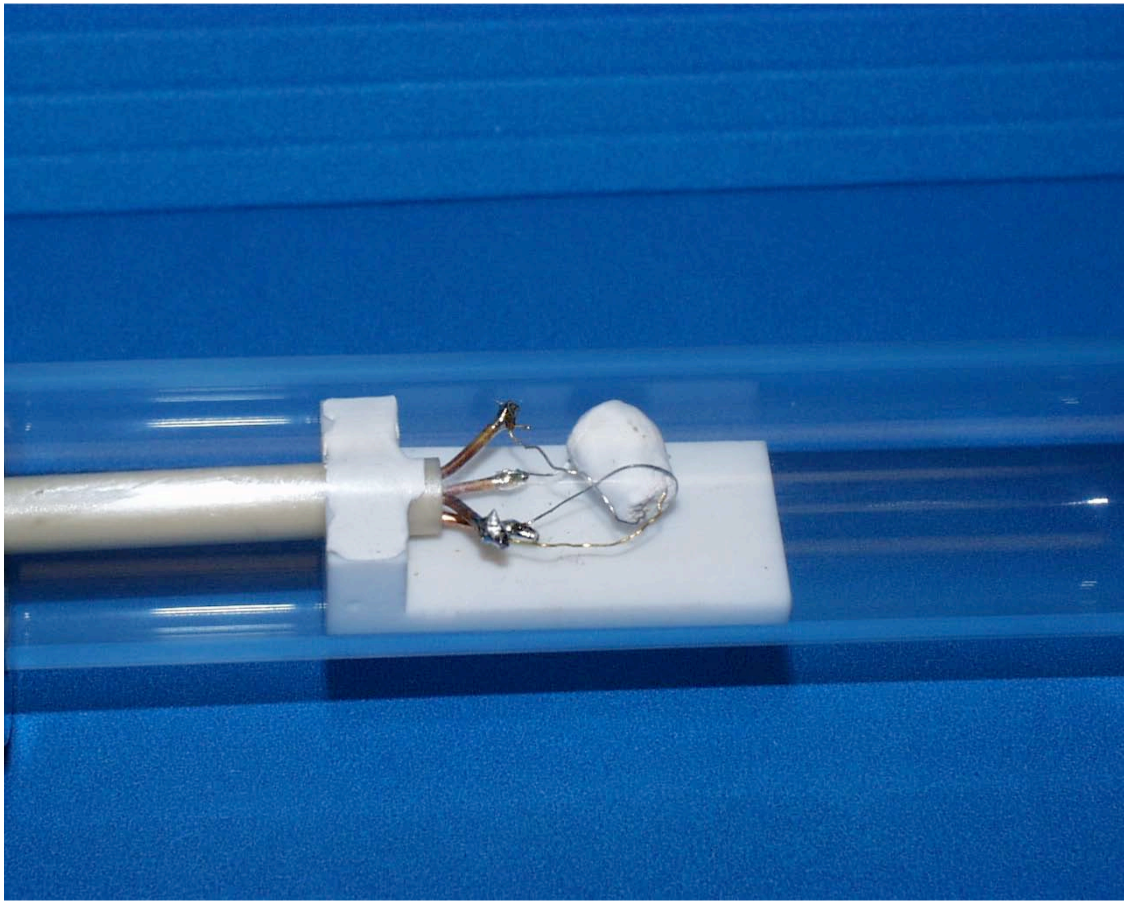
Bulk Preparation of $LaMCrO_3$ Electrode for Mixed Potential Sensors

- Commercial powder purchased from Praxair Corp.
- Lanthanum chromites made from spray pyrolysis process
- Electrode formed by isostatic pressing powder and sintering at 1650°C for 10 hours in air.
- Cube shape cut using a diamond saw.
- Pt wire embedded during sintering to make electrode for "bulk" type, mixed potential sensor.





Ceramic Sensor With Heater



Thin Film Sensor Development

- Thin film devices are more desirable than bulk ceramic devices
  - Low cost lithographic manufacturing techniques
  - Smaller sized
- Experimental
  - RF magnetron sputtering via oxide target
  - RF magnetron sputtering via fluoride target / precursor film
  - Electron beam and thermal evaporation
  - Pulsed laser deposition using fluoride and oxide composite targets
- Film Characterization
  - XRD, SEM, XRF characterization

Los Alamos
NATIONAL LABORATORY

RF Sputtering Using Fluoride Targets

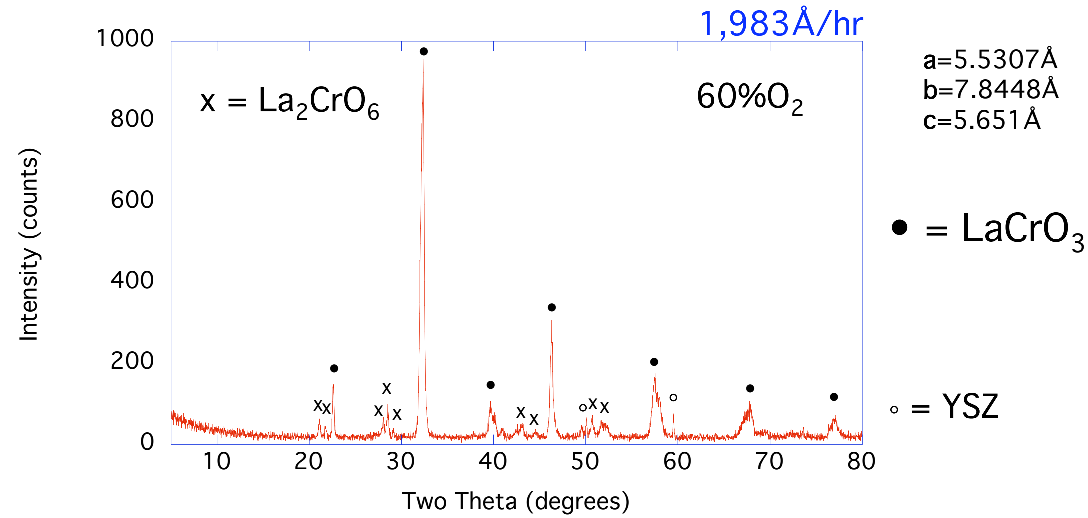
- Target fabricated using mixture of LaF_3, SrF_2, and Cr metal
- Ball-milled 6 hrs using alcohol and zirconia grinding media
- Powder was pressed into 2” diameter die and pressed at 400 lbs
- Target heated at 2°C/min in dry Ar to 1100°C and held for 500 min to sinter
- Sintered target was mounted to a 2” dia Cu sputter cup using Ag epoxy
- Poly-crystalline Al_2O_3, sapphire, or CeraFlex™ brand YSZ wafers were used as substrates
- Typical sputter conditions: 40 mTorr, UHP Ar 90° off axis, 125W RF
- Substrate temperature either left to float at ambient or 400°C

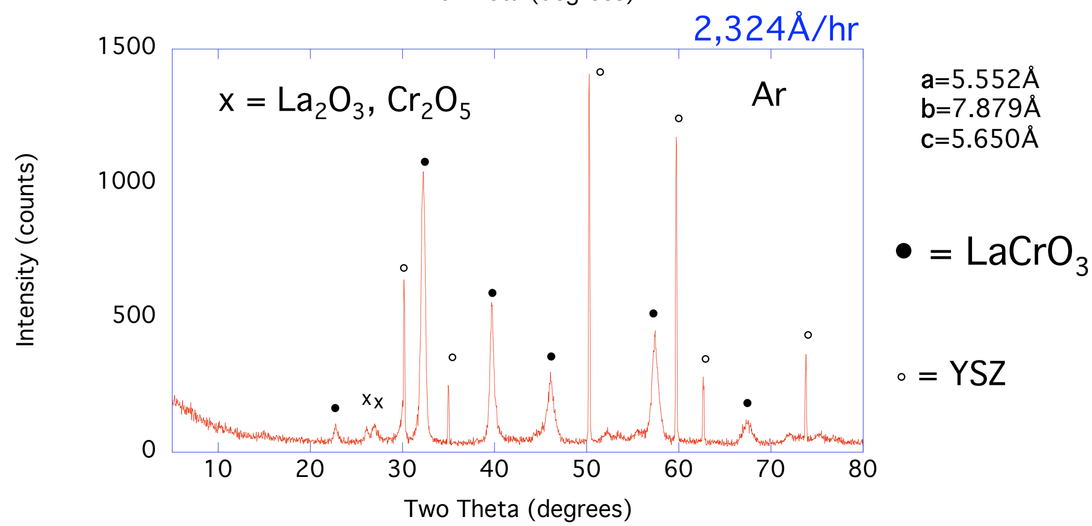
Los Alamos
NATIONAL LABORATORY

RF Magnetron Sputtering - Oxide Target Deposition

- CeraFlex™ brand YSZ wafers or polycrystalline Al_2O_3 and sapphire used as substrates.
- Commercial $La_{0.8}Sr_{0.2}CrO_3$ sputter target purchased from Praxair.

- Sputter conditions:
  - 40 mTorr sputter pressure
  - 60% O_2/Ar or UHP Ar
  - on-axis orientation to maximize deposition rate
  - 125W of RF power
  - T = 650°C



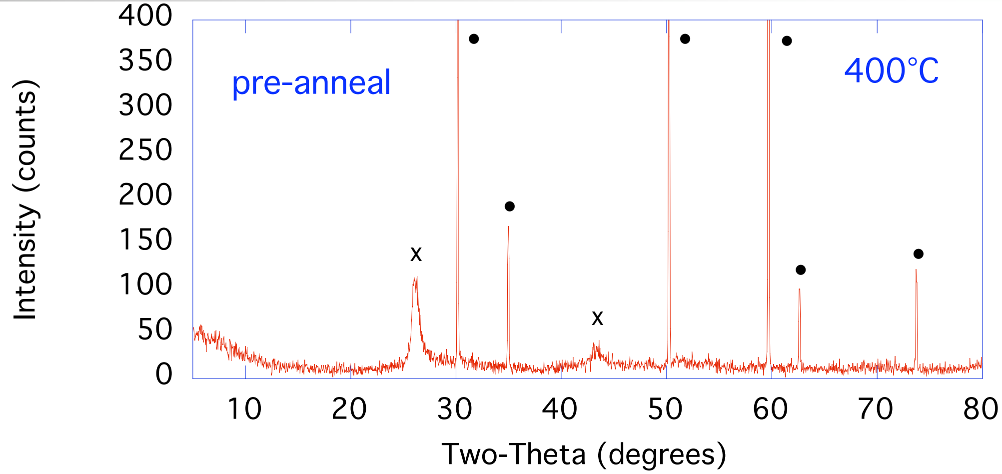


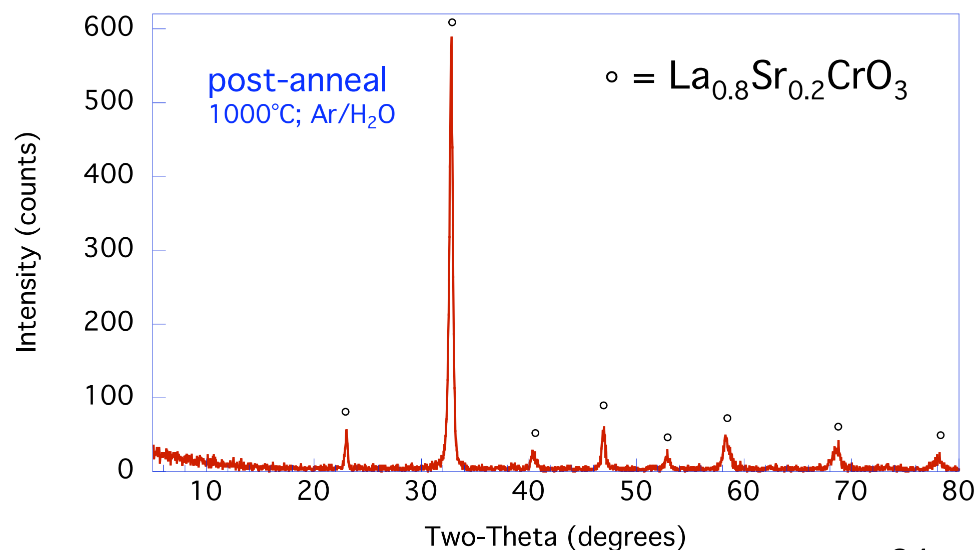
Los Alamos NATIONAL LABORATORY

RF Magnetron Sputtering - Fluoride Process

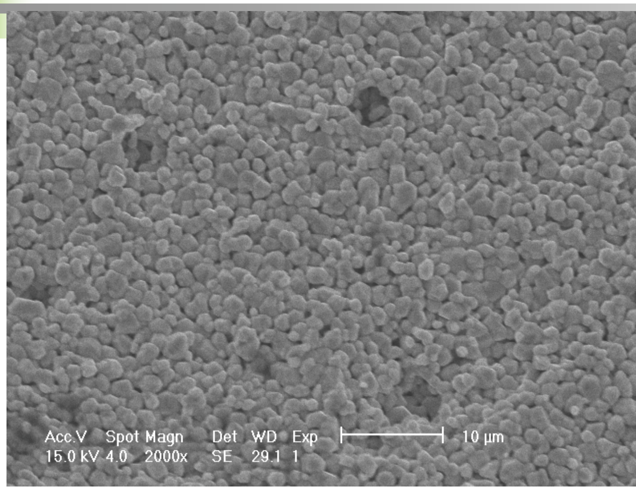
- Off-axis orientation required.
- Composite films deposited at 400°C exhibited good adhesion T_{sub} = 400°C
- Ar atmosphere, 40 mTorr
- 1.2μm (oxide thickness), 8 hrs deposition time
  - 1500Å/hr

- **a**=5.4523Å , **b**=5.4523Å **c**=13.443Å agrees well with literature data

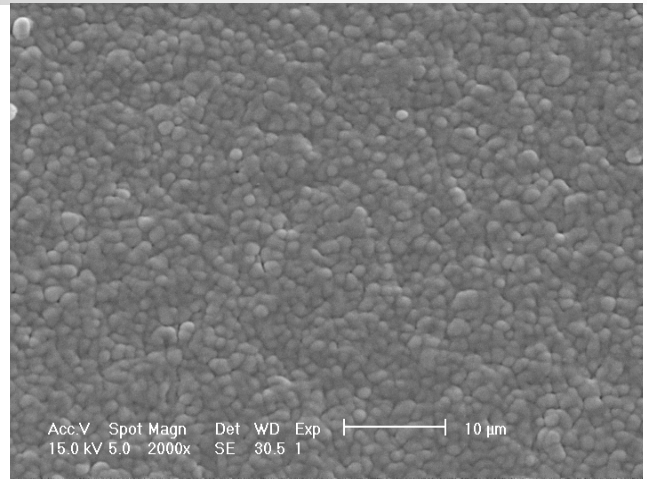




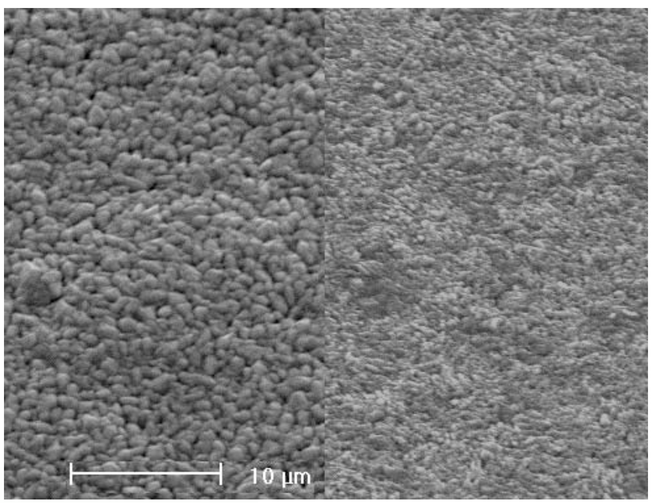
Thin Film SEM Analysis



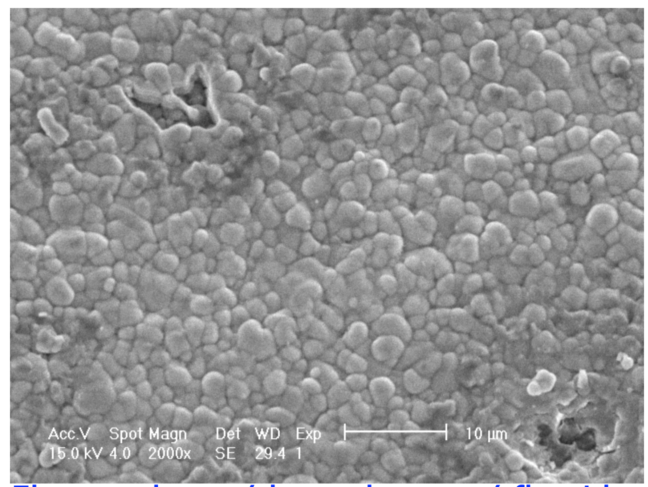
Bulk sintered material: 1650°C, 10hrs



RF magnetron sputtering / fluoride
400°C dep / 1000°C post anneal



RF magnetron sputtering / oxide
650°C deposition T / Ar

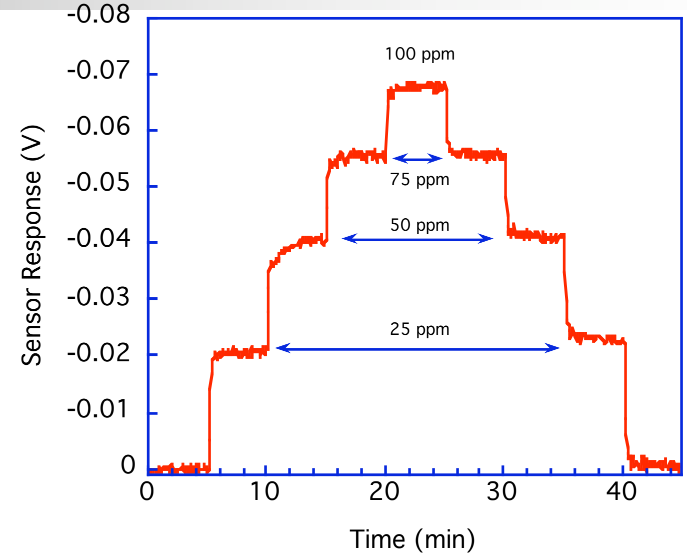


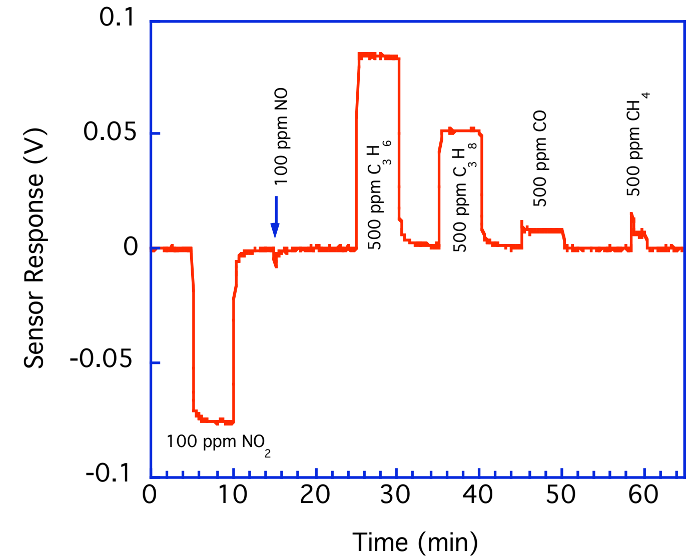
Electron beam/thermal evap. / fluoride
400°C dep / 1000°C post anneal

Los Alamos
NATIONAL LABORATORY

Thin Film Sensor Results

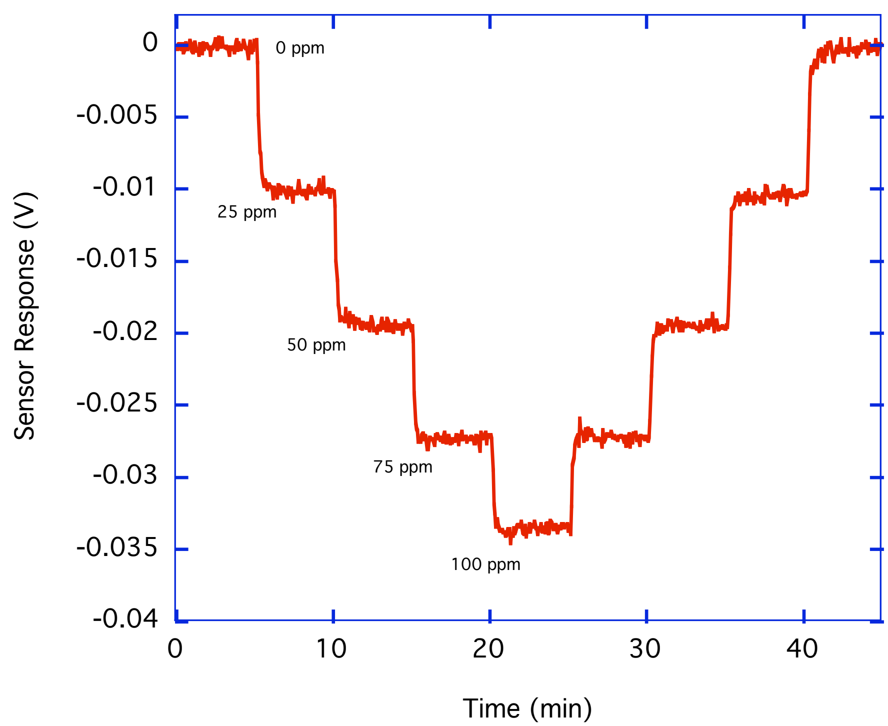
- Different metal oxide electrode selected based on observations of higher NO_x catalysis.
  - $LaCr_{0.8}Mg_{0.2}O_3$/YSZ/Pt
- Initial testing performed hot - 650°C and in 1%O_2
- Mixed potential response to NO_2 with no sensitivity to NO.
- Interference to CO and HC's
  - almost 5:1 sensitivity to NO_2





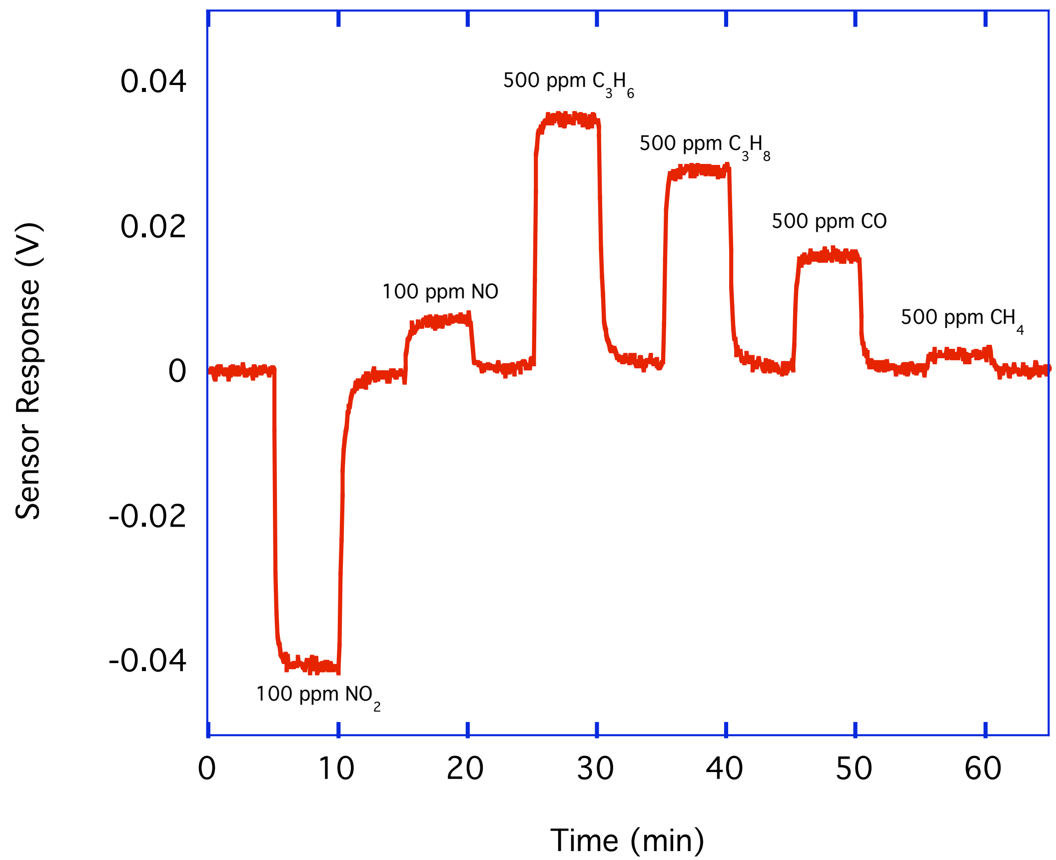
Response To Varying Levels of NO_2

- NO_2 response at 650°C, 10.4 % O_2/N_2 balance flowing at a base flow rate of 500 SCCM
- Reproducible response as gas concentration is stepped both up and down



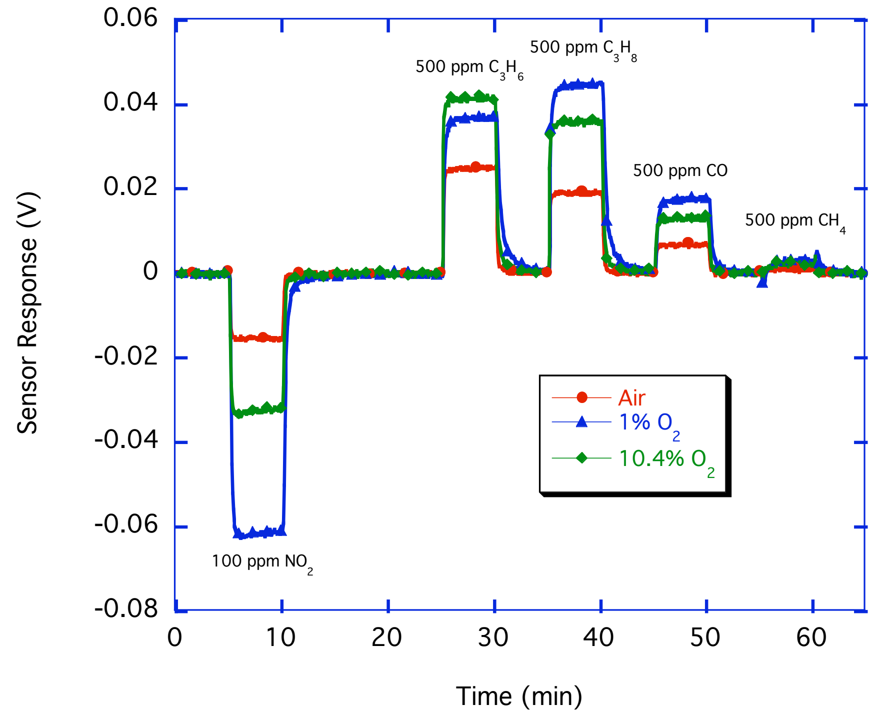
Thin Film Device Response 2000 hrs

- Thin film sensor $LaCr_{0.8}Mg_{0.2}O_3$/YSZ/Pt
- Sensor response to NO_2, NO, and selected HC's and CO versus time at 600°C after device testing at 650°C. Base gas is 10.4% O_2 at a flow rate of 500 SCCM.
- Response after 2000 hrs testing



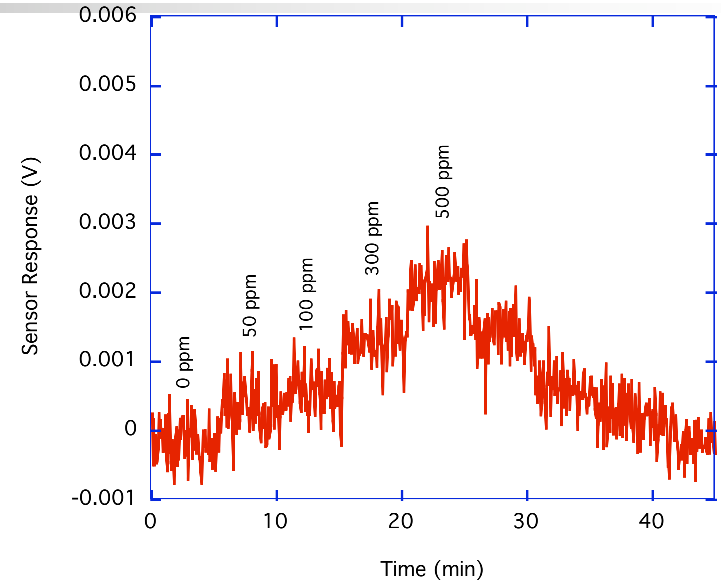
Oxygen Concentration Effects

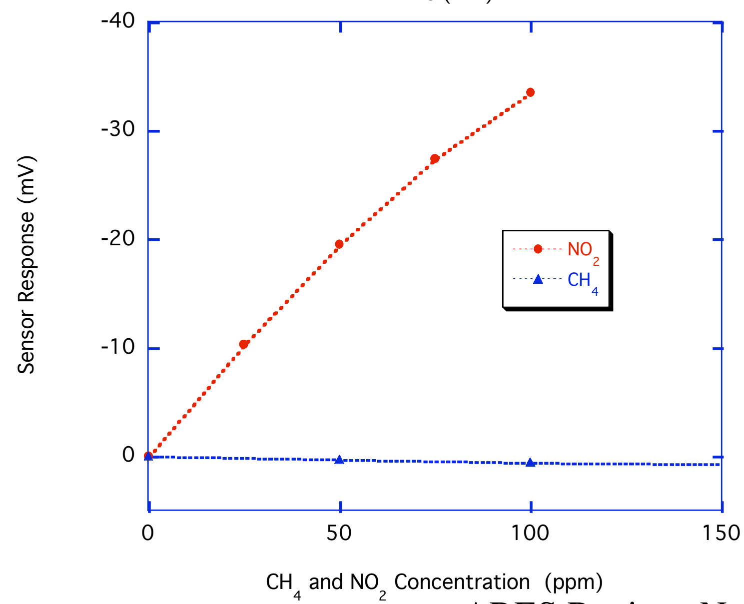
- Sensor response at 650°C
- Sensor response must be calibrated as a function of oxygen pressure
- Use lambda sensor to provide oxygen concentration



Methane Cross Interference Testing

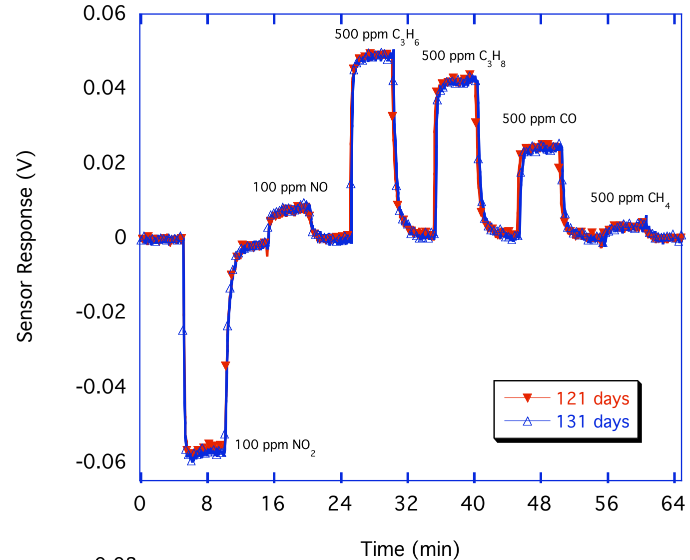
- CH_4 response at 650°C, 10.4 % O_2/N_2 balance flowing at a base flow rate of 500 SCCM.
- Almost no methane cross interference



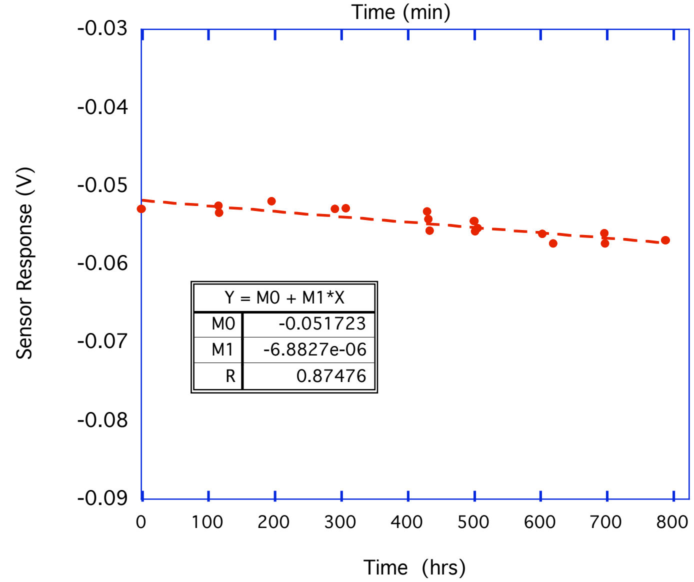


Long Term Testing

- Sensor response to NO_2, NO, and selected HC's and CO versus time at 121 and 131 days of lifetime testing at 600°C. Base gas is 10.4% O_2 at a flow rate of 500 SCCM



- NO_2 response for 800 hours of testing



Key Technical Barriers and Project Risks

- Key technical barriers are:
  - Designing sensors with adequate sensitivity and selectivity
  - Elimination of cross interferences
  - Response stability over sensor lifetime
    - Electrode ageing phenomena
  - Low cost requirements

Summary

- LANL NO_x sensor work commenced in February 2002
- Assembly of gas chromatography/mass spectroscopy system combined with a Horriba NO_x system complete
- Developed fabrication methods for both ceramic and thin film mixed potential based NO_x sensors
- Investigated nitric oxide and cross interference gas responses
  - Good sensitivity to NO_2
  - No CH_4 interference
- Investigation of long-term sensor response stability
  - Over 2000 hrs for some devices
- Preliminary contacts with sensor suppliers
  - Dephi, and Figaro USA
- Continuing sensor optimization work
- Development of theoretical models

Publications and Patents

- <u>Publications and Presentations</u>
  - F. H. Garzon, R. Mukundan and E. L Brosha "Solid State Ionic Devices For Combustion Gas Sensing" submitted to *Solid State Ionics* 2003
  - Eric L. Brosha, Rangachary Mukundan, David R. Brown, Q. X. Jia, Roger Lujan, and Fernando H. Garzon, "Techniques for the Thin Film Growth of La1-xSrxCrO3 for Solid State Ionic Devices," submitted to *Solid State Ionics*, July 2003.
  - Eric L. Brosha, Rangachary Mukundan, and Fernando H. Garzon, "The Role of Heterogeneous Catalysis in the Gas-Sensing Selectivity of High-Temperature Mixed Potential Sensors," proceedings of the 202nd meeting of the Electrochemical Society, Salt Lake City, Utah, October 21-25, 2002.
  - Fernando H. Garzon, Eric L. Brosha, Rangachary Mukundan,"The Evolution of High Temperature Gas Sensors," presented at the 201st meeting of the Electrochemical Society, Philadelphia. May 2002.

- Patents
  - S-99,902 - ELECTRODES FOR SOLID STATE GAS SENSOR Patent granted
  - S-100,655 - THIN FILM MIXED POTENTIAL SENSORS-Patent disclosure in Process of filing

Los Alamos NATIONAL LABORATORY